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# OF A CH-Be ALLOY

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# HIGH TEMPERATURE X-RAY STUDIES OF A Cu-Be ALLOY

by

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Lieutenant, United States Navy

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN MATERIALS SCIENCE

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#### **ABSTRACT**

The Debye-Scherrer method has been used to study the sequence of precipitation structures in a two percent beryllium-copper alloy. A special x-ray camera fitted with a furnace was used to follow the age-hardening process at controlled elevated temperatures. It is concluded that no intermediate structure exists which is capable of three dimensional diffraction. Two earlier investigations of this system suggest the existence of intermediate structures. It is shown in this paper that these intermediate structures are actually oxides of beryllium-copper. Existing confusion regarding the correct lattice parameters of the alpha and beta prime phases has been eliminated with the determination of their precise values.



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#### 1. Introduction.

Copper rich beryllium-copper alloys exhibit a high degree of hardenability. The proposed mechanism for precipitation age hardening of these alloys has been the subject of five important investigations [4,5,7,8,9]. Although the details of the process are not agreed upon, a general understanding of atom movement and structural change may be envisaged.

A recent revised constitution diagram of copper rich beryllium alloys is presented in Fig. 1. The types of structures which occur in this system are: alpha phase, face-centered cubic; beta phase, disordered body-centered cubic; beta prime phase, body-centered cubic. The author shall attempt to remain consistent with these designations. In referring to earlier works, phases will be designated in accordance with Fig. 1 and will be followed by the reported designation in parentheses.

The system is an example of discontinuous precipitation. It has been found<sup>3</sup> that precipitation of the beta prime (gamma) phase is apparent after aging the solution-quenched alloy for seven hours at 300°C. When the alloy is aged at 400°C this structure becomes apparent after only one hour. However when aged at 200°C the beta prime (gamma) phase did not appear even after 1100 hours.

Hansen, M. Constitution of Binary Alloys. McGraw-Hill, 1958: 282.

<sup>&</sup>lt;sup>2</sup>Ibid., p. 283.

<sup>&</sup>lt;sup>3</sup>Gruhl, W. and G. Wasserman. Uber den Verlauf der Asscheidung bei Kupfer-Beryllium-Legierungen. Metall, v. 5, March, 1951: 141.



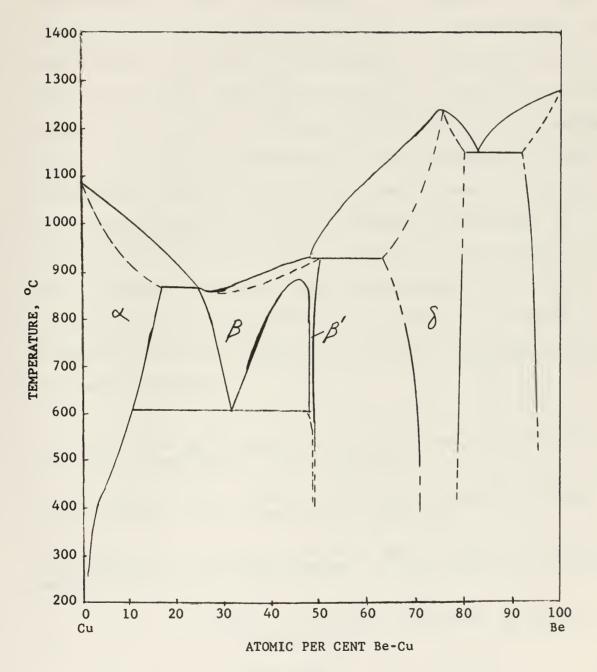


Fig. 1



Guinier and Jacquet found evidence of the formation of Guinier-Preston zones<sup>4,5</sup> composed of Be atoms. These zones appeared to be co-. herent with the (100) planes of the alpha phase. 6 Recently this has been confirmed by electron microscopy. A 2% Be-Cu alloy was aged for thirty minutes at 300°C. It was found that the striations, seen when examining Be-Cu alloys metallographically, and the Guinier-Preston zones were identical. These zones were interpreted as consisting of Be atoms which had formed into thin platelets parallel to the (100) planes of the parent or alpha structure. It is well worth stressing the above emplanation for the presence of the striations. These microscopically observable parallel streaks or lines have often been confused with twinning. The fact that copper twins easily has increased this confusion. In addition, the electron microscope study detected an anti-periodicity of the (100) planes of the parent matrix, indicating that the lattice was strained. This would imply that copper beryllium alloys are strainhardened. This method for hardening had previously been decided upon by Guy, Barrett, and Mehl.8

<sup>&</sup>lt;sup>4</sup>Guinier, A. and P. Jacquet. On the Age-Hardening of Copper-Beryllium Alloys. Comp. Rend. v. 217, 1943: 22-24.

<sup>&</sup>lt;sup>5</sup>Guinier, A. and P. Jacquet. Etude du Durcissement des Alliages Cuivre-Glucinium. Rev. de Metall. v. 41, 1944: 1-16.

<sup>&</sup>lt;sup>6</sup>Guy, A. G., C. S. Barrett, and R. F. Mehl. Mechanism of Precipitation in Alloys of Beryllium in Copper. A.I.M.E. Tech. Pub. No. 2341, New York meeting, Feb., 1948: 3.

Tanaka, K., M. Mannami, K. Izumi, and K. Marikawa. Structure of G.P. Zone in Cu-2% Be Alloy. Acta Meta., v. 11, Jan., 1963: 79.

<sup>&</sup>lt;sup>8</sup>Guy, A. G., C. S. Barrett, and R. F. Mehl, op. cit., p. 1.

Geisler, Mallery, and Steigert<sup>9</sup> studied the progressive precipitation using single crystals of 1.73% Be-Cu. They found five reflections which could not be attributed to the matrix structure when the crystals were aged for 18 hours at 300°C. They deduced that this beta double prime (gamma prime) phase had a body-centered tetragonal structure. In order to obtain this structure a prior structure designated beta triple prime (gamma double prime) was postulated from the diffraction effects noted earlier by Guinier and Guy. <sup>10</sup> They decided that these two intermediate structures were coexistent, but that the overall process would probably proceed as shown in Fig. 2. <sup>11</sup>

Gruhl and Wasserman<sup>12</sup> have reported one intermediate structure, which is coherent with the matrix lattice. They used the Debye-Scherrer polycrystalline method for conducting their study. Using wires of 1.82% Be-Cu they found three new lines appearing in the diffraction pattern. They decided that a body-centered tetragonal structure accounted for these lines. Their overall proposed mechanism is pictured in Fig. 3. This was the first time a structure capable of three dimensional diffraction had been reported.

There are several interesting discrepancies about the findings of Gruhl and Wasserman and that of Geisler, Mallery, and Steigert. 13 For

<sup>&</sup>lt;sup>9</sup>Geisler, A. H., J. H. Mallery, and F. E. Steigert. On the Mechanism of Precipitation in Copper-Beryllium Alloys. Journal of Metals, v. 4, March, 1952: 309.

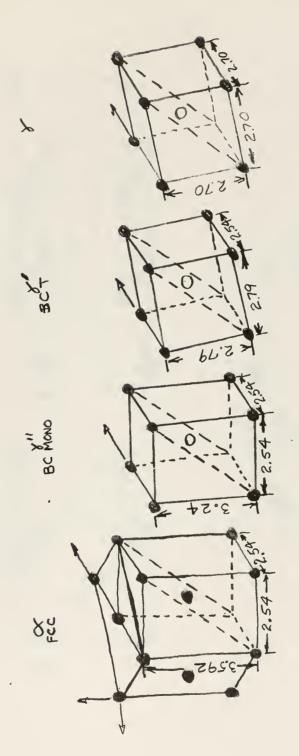
<sup>&</sup>lt;sup>10</sup>Ibid., p. 311.

<sup>&</sup>lt;sup>11</sup>Ibid., p. 315.

 $<sup>^{12}</sup>$ Gruhl, W. and G. Wasserman, op. cit., pp. 142-143.

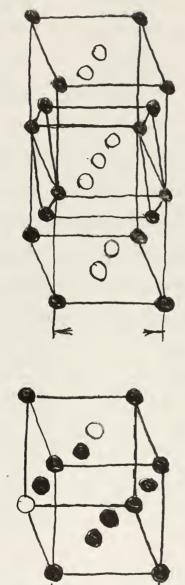
<sup>13</sup>Hardy, H. K. and T. J. Heal. Report on Precipitation. Progress in Metal Physics, v. 5, Pergamon, 1954: 220.

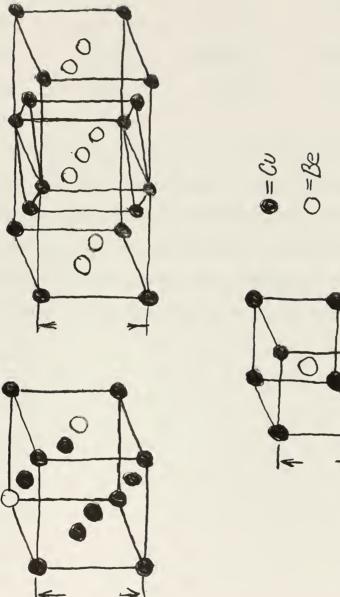


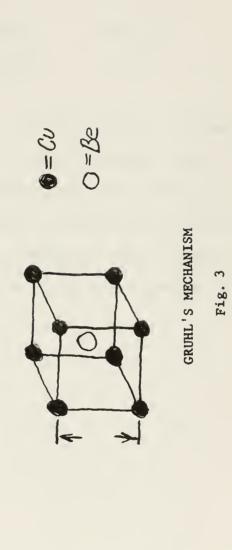


GEISLER'S MECHANISM











ease in comparison these differences are listed in Table 1. The initials of the surnames are used to distinguish their respective findings.

Table 1

| Phase   | Structure | G-W         | G-M-S       |
|---------|-----------|-------------|-------------|
| Alpha   | F.C.C.    | 3.54 Å      | 3.592 Å     |
| Beta '' | B.C.T.    | 2.50/3.54 Å | 2.54/2.79 A |
| Beta '  | B.C.C.    | 2.67 A      | 2.70 Å      |

The objectives of this research are to refine the lattice parameters of the alpha and beta single prime phases of beryllium-copper alloys and to determine the structure of any intermediate precipitate structure.

The proposed means for the investigation of this system was the use of the Debye-Scherrer method using a high temperature camera in order to study the continuous course of precipitation in the copper rich beryllium system.



### 2. Experimental Procedure.

High temperature camera. The first practical Debye-Scherrer high temperature camera was originally described by N. W. Buerger. 14,15 The model used in this research was manufactured by Otto von der Heyde; details of the camera are pictured by Klug and Alexander. 16 It was coupled with a standard x-ray generating machine made by North American Philips Co. Inc. The source of energy for the camera's furnace was a voltage/current regulated direct current power supply. It was manufactured by Kepco Inc., Mod. ck18-3. This supply proved to be constant during long extended operating periods. A schematic drawing of the electrical circuit used is shown in Fig. 4. The ampere and voltage meters were made by Weston. Fig. 5 shows the components hooked up and operating.

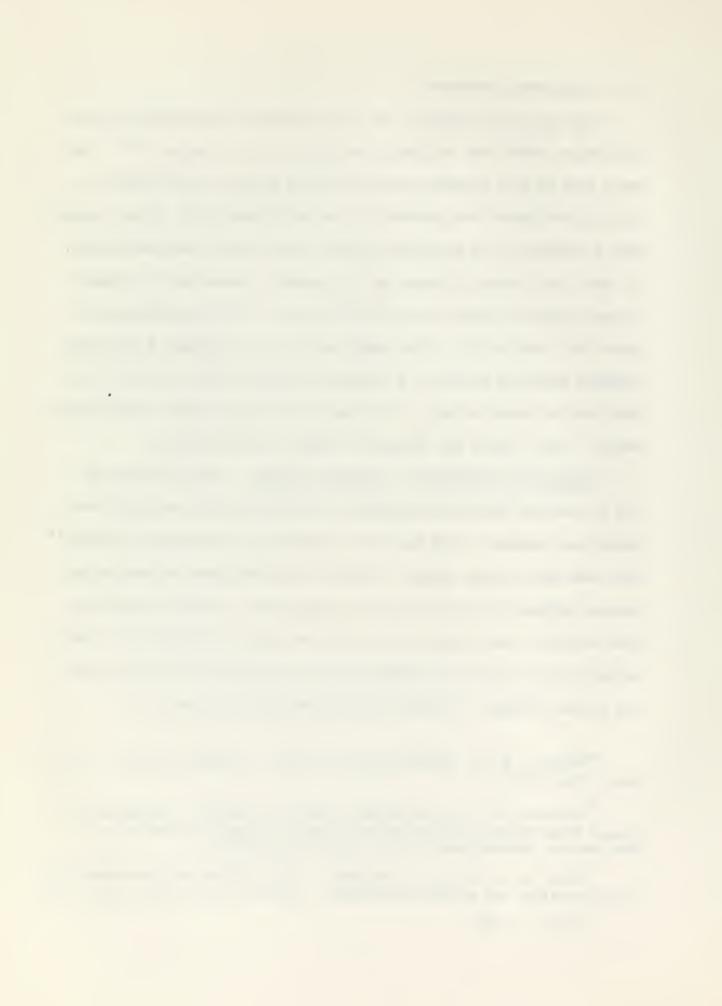
Temperature calibration of camera's furnace. The calibration of the furnace was initially attempted by using materials, inorganic compounds and elements, which had known temperature transformation points; 17 also used were various organic compounds which had known melting points. Several difficulties were encountered immediately. Purity of the samples available, and encapsulation of the materials into fine pyrex capillaries with allowances for differences in coefficients of expansion were two of the problems. In some cases the materials were not only

<sup>14</sup> Buerger, N. W. The Chalcocite Problem. Economic Geology, v. 36, Jan., 1941: 19-44.

<sup>15</sup> Buerger, M. J., N. W. Buerger, and F. G. Chesley. Apparatus for Making X-Ray Powder Photographs at Controlled Elevated Temperatures. The American Mineralogist, v. 28, May, 1943: 285-302.

<sup>16</sup>Klug, H. P. and L. E. Alexander. X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials. New York: John Wiley, 1954: 227.

<sup>17&</sup>lt;sub>Ibid., p. 229.</sub>





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Fig. 0. Laimont Laguat.



hydroscopic but, in fact, were explosive in nature. After a great deal of time and effort a very rough curve expressing temperature as a function of power input was obtained. The use of thermistors was consequently considered. Although quite accurate for limited temperature ranges, it was found that thermistors have a high temperature limitation. The use of a thermocouple followed. By using a chromel-alumel thermocouple, errors no greater than plus or minus 2.2°C were to be expected. 18 The small size of the furnace, about one quarter of an inch in diameter, caused some concern as to the loss of heat due to conduction of the thermocouple wires themselves. Thermal conductivities for chromel and alumel were found to be no greater than 0.071 cal/sec/cm<sup>2</sup>/cm/°C, 19 and were therefore acceptable.

Another method of calibration offering greater accuracies of plus or minus 0.1% was considered. This procedure 20 uses an internal standard of platinum. The platinum used should have a purity of at least 99.999% and should be carefully annealed at 2000°F before using. By measuring the lattice expansion of the platinum which is face-centered cubic, the temperature of the metal may be determined. This method has been used with success. 21 However, the availability and cost of the material were such that it was decided to tolerate the larger errors of

<sup>18</sup> Caldwell, F. R. Thermocouple Materials. N.B.S. Monograph No. 40, Government Printing Office, Washington, D. C. March, 1962: 17.

<sup>&</sup>lt;sup>19</sup>Personal correspondence of the author, letter from R. K. Kirby, National Bureau of Standards, July 10, 1964.

<sup>20</sup> Caldwell, F. R. op. cit., p. 22.

<sup>&</sup>lt;sup>21</sup>Quader, A. and B. N. Dey. Lattice Expansion and Debye Temperature of A-Phase Ag Cd Alloys. Indian Journal of Physics, v. 36, Jan., 1962: 43-54.



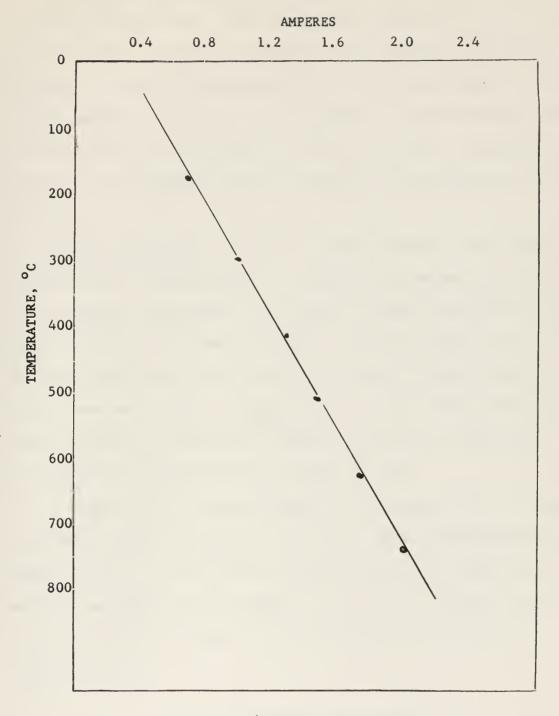
a thermocouple. The wires used to make the thermocouple were B&S 28 gage and were manufactured by Leeds and Northrup. The resulting curve was very satisfactory, Fig. 6.

Problem with high background intensity. Operation of the camera disclosed the problem of collimating the copper radiation used. A comparison of the collimator of the high temperature camera and the collimator of a normal camera was made. The size of the pinholes (inside diameters) of the collimators was 0.5mm and 0.35mm respectively. The air paths (double the distances between the exit ports of the collimators and the location of the material to be x-rayed) were 1.26 inches and 0.468 inches respectively. The greater the air scattering path and the larger the pinhole, the higher the background intensity of the film. The background intensity should be kept as low as possible so that the films can be correctly measured.

The first attempt to solve this problem dealt with the monochromation of the radiation using a suitable crystal. A fluorite crystal which was cleaved parallel to the (111) plane was used. This crystal has good stability  $^{22}$  and its use provides the separation of the copper radiation into its component parts. The  $K_b$ , and nearly all of the white radiation were eliminated, and the darkening of the background of the films disappeared when this technique was employed. However, the intensity of the  $K_{a1}$  and  $K_{a2}$  beams was reduced to the extent that exposure times of one hour or more were required to produce diffraction lines easily visible. Because of this increase in exposure time another solution was sought.

Lipson, H., J. B. Nelson and D. P. Riley. Monochromatic X-Radiation. Journal of Scientific Instruments and of Physics in Industry, v. 22, Oct., 1945: 184-187.





TEMPERATURE/CURRENT RELATIONSHIP

Fig. 6



Ordinarily copper radiation is filtered using a nickel foil which is 0.021 of an inch thick. This filter reduces the ratio of  $K_b$  to that of  $K_a$  to 1/600. In addition it greatly reduces the white radiation. <sup>23</sup> The use of a second foil shielding the film itself was suggested to me by N. W. Buerger. Two small strips of nickel foil were obtained. The foil was 0.0007 of an inch thick. The use of this foil eliminated almost all of the background, and the exposure time was maintained at ten minutes.

Specimen preparation. In order to obtain suitable Be-Cu alloys for experimentation, correspondence was initiated with The Beryllium Corporation of Reading, Pennsylvania. The result of several letters was that powdered alloys were extremely difficult to produce because of the oxidation of the surface area. In addition, wires of 0.5mm in diameter and smaller were not available. However, some very thin foil material would become available in January 1965, and some would be sent when ready.

The foil has not been received as of April 23, 1965.

A section of flat plate was found to be on hand at the U. S. Naval Postgraduate School in Monterey, California. It had been purchased from BERYLCO in 1955. It was solution treated plus 37% cold rolled. The analysis was supplied by the company. 24 It is: Be-2.00,Co-0.22,Fe-0.14, Si-0.12,Al-0.03,Zn-0.03,Ag-0.01,Sn-0.01,Cr-0.01,Pb-0.00,Cu-balance (weight percent).

Azaroff, L. V. and M. J. Buerger. The Powder Method in X-Ray Crystallography. McGraw-Hill, 1958: 34.

<sup>&</sup>lt;sup>24</sup>Personal correspondence of the author, letter from A. E. Goldberg, University of California, Lawrence Radiation Laboratory, April 1, 1965.



A powder of this alloy was prepared by slowly grinding the plate with a jeweler's file. The powder was then annealed in an air furnace for one half hour at 820°C. The quenched powder was dried and screened through doubled 400 mesh bolting cloth. It was then placed into a thin walled pyrex capillary tube. The resulting diffraction film showed spotty lines indicating that the particle size was too big. Further observation led to the conclusion that the powder was oxidized both from the filing and from the heat treatment. A more suitable forming method was then decided upon.

It was decided to draw wires from the flat plate. The plate was first cut into a rectangular rod three inches in length and one quarter inch on each side. This billet was then ground into a round rod about 1.75mm in diameter. The end of the rod was pointed so as to protrude through the first hole of a steel draw plate, Fig. 7. The pointed end of the wire was clamped in a vice and the draw plate pulled over the wire, thus reducing the wire's diameter. Eighteen reductions were needed to obtain a wire with a diameter of 0.54mm. After each third reduction it became impossible to continue until the wire had been heated above its recrystallization point, thereby removing the work hardening effect.

When a diffraction pattern of this wire was attempted the resulting lines were so weak and indistinct, it was decided that the grain size was much too large. Fig. 8 illustrates the grain size.

Three rods were cut and ground to an initial diameter of about

1.7mm. They were annealed at 820°C for one half hour and then reduced

50% (four reductions). The fourth reduction became possible by lubricating the wire with common soap. This procedure was repeated once more



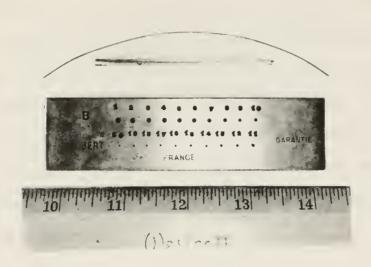


Fig. 7.
Wires and Draw Plate



and then for the penultimate heat treatment the wires were reduced 60% (five reductions) and the annealing temperature lowered to  $775^{\circ}$ C. The final heat treatment was essentially the same as the penultimate except that the time was reduced from thirty to fifteen minutes. A substantial reduction of grain size was achieved by this method, Fig. 9. Each heat treatment was followed by pickling the wires in a solution of  $H_2SO_4$ ,  $H_2O_2$ ,  $HC_2H_3O_2$  and  $H_2O_2$ . The pickling removed the surface oxides acquired in the heat treatment furnace. The diffraction patterns now showed solid lines with high intensity.

 $<sup>^{25}</sup>$ Lyman, T., Editor, Metals Handbook, v. 2, American Society for Metals, 1964: 642.





Fig. 8.
Alpha Proce, lorge grain size.

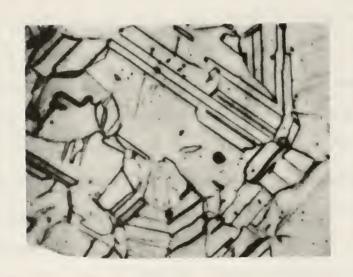


Fig. 9.
Alpha Phase, small grain size.



## 3. Results.

While preparations for x-ray studies were being effected, 13 specimens cut from the flat plate were solution annealed and then aged at  $300^{\circ}$ C. A hardness curve was obtained and is shown in Fig. 10. Note that the curve reached a maximum Rockwell 'A' hardness of 71.5 in ten hours and that it was essentially the same after 236 hours. Since this temperature is close to the division between optimum and over-aging temperatures, it was decided to age the specimens in the camera at 200, 300 and  $425^{\circ}$ C.

The first objective was to determine the structure of the alpha phase. The initial specimen studied was in the solution quenched condition. The structure was found to be face-centered cubic. Its lattice parameter was determined to be 3.585  $^{\circ}$ A. Table 2 shows the comparison of observed and calculated values for the structure using this lattice parameter.  $A_{\circ}$  was obtained by plotting the values of A observed for each line against the function,  $\cos^2\theta$ . Theta in this expression is the observed Bragg angle. The details of this procedure are outlined by Azaroff and Buerger. In brief this method refines the value of  $A_{\circ}$  by extrapolation to an angle of  $90^{\circ}$  where errors are reduced to a minimum.

As the specimen used to determine the alpha phase was subjected only to room temperature (20°C), it could then be aged at 425°C. After nine hours the aging was terminated. Films taken during the aging process showed that several new lines had appeared. Afterwards the specimen was photographed using another camera (one without the furnace). The new lines were used in attempting to obtain the structure of the

<sup>&</sup>lt;sup>26</sup>Azaroff, L. V. and M. J. Buerger, op. cit., p. 235.



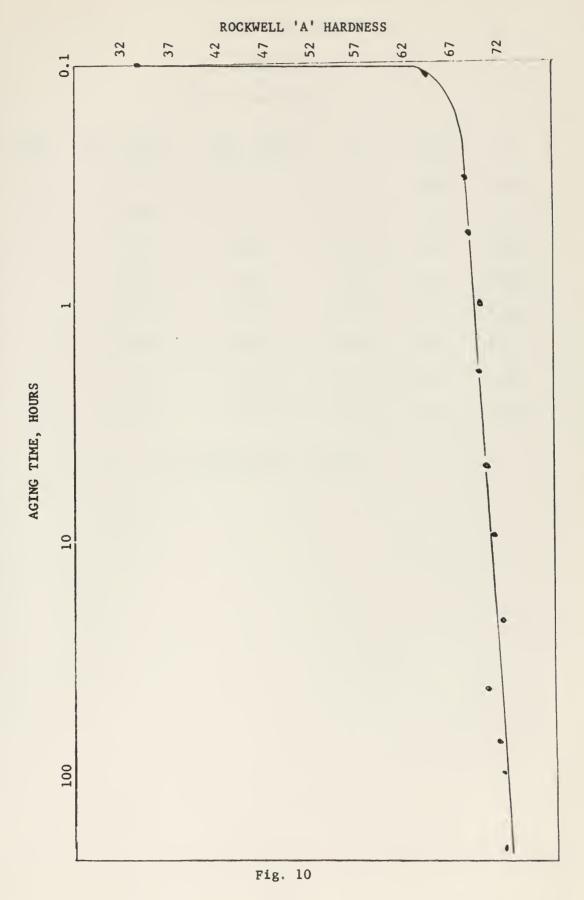




Table 2
Alpha Phase Cu-2% Be

| Line | OBS. SIN O | CALC. SIN 0 | h k 1 | I/I <sub>o</sub> | Å     |
|------|------------|-------------|-------|------------------|-------|
| 1    | 0.377      | 0.372       | 1 1 1 | 100              | 3.531 |
| 2    | 0.433      | 0.429       | 2 0 0 | 52               | 3.543 |
| 3    | 0.610      | 0.607       | 2 2 0 | 41               | 3.566 |
| 4    | 0.716      | 0.712       | 3 1 1 | 74               | 3.566 |
| 5    | 0.749      | 0.744       | 2 2 2 | 22               | 3.560 |
| 6    | 0.862      | 0.859       | 4 0 0 | 20               | 3.574 |
| 7    | 0.937      | 0.936       | 3 3 1 | 105              | 3.581 |
| 8    | 0.961      | 0.961       | 4 2 0 | 83               | 3.582 |

A<sub>o</sub> Extrapolated = 3.585 Å



beta prime phase. The structure could not be found when all these new lines were used. Unfortunately no alloy was available which had a composition of 49% Be by weight. Such an alloy would have been composed solely of beta prime (see Fig. 1) and the determination of the structure would have been simple in comparison. After considerable effort it became apparent that some of these new lines were due not to an internal structure of the alloy, but in fact, were the result of a surface film corrosion. When the wire was pickled again the extraneous lines were eliminated leaving only those of the alpha and beta phases. The structure was determined to be body-centered cubic (CsCl type). The lattice constant was refined by the extrapolation method already mentioned. The value obtained was 2.699 A. Table 3 shows the comparison of the observed and calculated values of the Bragg angles. In addition, the depleted alpha phase lattice parameter was determined from this film, Table 4. The value calculated, 3.608 A, is seen to have approached the generally known value of pure copper, 3.615 A. This is the expected result. When examined microscopically the wire showed the over-aged condition, Fig. 11. Note that the beta prime phase has precipitated to such a great extent as to be noticed in every grain.

A second wire in the solution-quenched condition was then aged in the camera's furnace at 300°C. After 12 hours the lines corresponding to the matrix (420) and (331) planes were seen to have become diffused and weakened. This broadening has been noticed by investigators in the past. 27,28 The most accepted conclusion is that this indicates the

<sup>&</sup>lt;sup>27</sup>Gruhl, W. and G. Wasserman, op. cit., p. 141.

<sup>&</sup>lt;sup>28</sup>Dahl, O., E. Holm, and G. Massing. X-Ray Investigation of the Age-Hardening in Beryllium-Copper Alloys. Beryllium, Its Production and Application, Reinhold, 1932: 213.



Table 3. Beta Prime Phase Cu-2% Be

| Line | <u>Obs. sin θ</u> | Calc. sin 0 | <u>h k 1</u> | A     |
|------|-------------------|-------------|--------------|-------|
| 1    | 0.291             | 0.285       | 1 0 0        | 2.642 |
| 2    | 0.408             | 0.404       | 1 1 0        | 2.667 |
| 3    | 0.498             | 0.494       | 1 1 1        | 2.674 |
| 4    | 0.573             | 0.570       | 2 0 0        | 2.655 |
| 5    | 0.642             | 0.638       | 2 1 0        | 2.682 |
| 6    | 0.702             | 0.699       | 2 1 1        | 2.684 |
| 7    | 0.810             | 0.809       | 2 2 0        | 2.687 |
| 8    | 0.903             | 0.903       | 3 1 0        | 2.696 |

 $A_0$  Extrapolated = 2.699 A

Table 4. Depleted Alpha Phase

| Line | <u>Obs. sin θ</u> | Calc. sin 0 | <u>h k 1</u> | A     |
|------|-------------------|-------------|--------------|-------|
| 1    | 0.377             | 0.370       | 1 1 1        | 3.531 |
| 2    | 0.433             | 0.427       | 2 0 0        | 3.552 |
| 3    | 0.610             | 0.604       | 2 2 0        | 3.570 |
| 4    | 0.715             | 0.708       | 3 1 1        | 3.572 |
| 5    | 0.746             | 0.740       | 2 2 2        | 3.575 |
| 6    | 0.858             | 0.854       | 4 0 0        | 3.589 |
| 7    | 0.933             | 0.931       | 3 3 1        | 3.597 |
| 8    | 0.956             | 0.955       | 4 2 0        | 3.605 |

 $A_0$  Extrapolated = 3.608  $\stackrel{\text{o}}{A}$ 

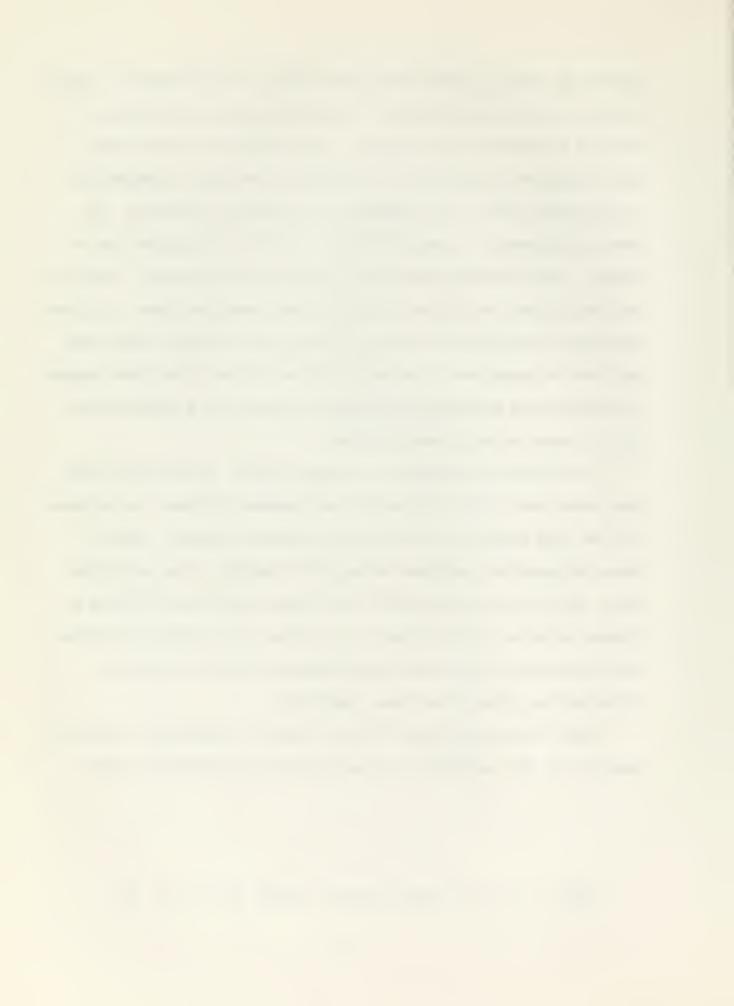


lattice has become strained during the process of precipitation. 29 After 38 hours two new lines appeared. When the aging time had increased to 60 hours an additional line appeared. After 159 hours the only subsequent change was the increase of broadening of the lines corresponding to the parent matrix. Age hardening was curtailed at this time. The wire was transferred to another camera as before, and a pattern was obtained. This film showed that in all, nine lines had appeared. The wire was then pickled, and another diffraction photograph was taken. The pickling process removed all but one of the new lines, and this single line was found to correspond to the beta prime precipitate. The lines removed by pickling were considered to have been the result of a surface oxide.

A third wire was selected to be aged at 200°C. After 22 hours the high index lines of the alpha matrix were becoming diffused. At 56 hours all the lines except the (111) were very weak and diffused. After 75 hours the aging was terminated without the recording of one new reflection. The wire was then observed to be almost free from the effects of thermal corrosion noted previously. As before, room temperature diffraction pictures were taken, and three additional lines were detected. After pickling, these three lines disappeared.

Other attempts were made to find a transition structure. Wires were aged at 169, 294, and 305°C. No new precipitate structure was found.

<sup>&</sup>lt;sup>29</sup>Guy, A. G., C. S. Barrett and R. F. Mehl, op. cit., p. 22.





Pig. 11.
Overaged Gu-De Alloy



Fig. 12.



## 4. Discussion of Results.

The lattice constants for the alpha and beta prime phases are listed in Table 5, and may be compared with the reported values listed in Table 1, reproduced here.

Table 5

| Phase  | McHugh  | G-W    | G-M-S   |
|--------|---------|--------|---------|
| Alpha  | 3.585 Å | 3.54 A | 3.592 Å |
| Beta ' | 2.699 A | 2.67 Å | 2.70 Å  |

It is evident that the constants obtained by the author agree closely with those reported by Geisler, Mallery and Steigert.

The results found from aging the Be-Cu wires give no indication that a transition structure grows to produce three dimensional diffraction. This result coupled with the observations concerning the broadening of the high index lines of the parent structure are in accord with the findings of Guy, Barrett, and Mehl. 30

The <u>d</u> spacings and Bragg angles for the first nine lines of the oxide film structure are listed in Table 6. Given also are the lines which Gruhl and Wasserman and Geisler, Mallery and Steigert used in finding their intermediate structures. Because the radiation which these investigators used was not given, their results are listed in the form in which they were reported. 31,32

<sup>30</sup>Guy, A. G., C. S. Barrett and R. F. Mehl, op. cit., p. 4.

<sup>31</sup>Gruhl, W. and G. Wasserman, op. cit., p. 142.

 $<sup>^{32}</sup>$ Geisler, A. H., J. H. Mallery and F. E. Steigert, op. cit., p. 311.



Table 6

| G-W    | McHu   | gh      | G-M-S  |
|--------|--------|---------|--------|
| 17.66° | 16.75° | 2.673 A | 2.78 Å |
| 28.50° | 18.15° | 2.472 Å | 2.54 Å |
| 31.58° | 19.75° | 2.279 Å | 1.97 A |
|        | 24.67° | 1.845 Å | 1.86 Å |
|        | 27.17° | 1.686 Å | 1.56 % |
|        | 29.50° | 1.564 A |        |
|        | 31.15° | 1.487 A |        |
|        | 33.35° | 1.401 Å |        |

There is no positive correspondence between the angles that Gruhl and Wasserman report, and those that the author has obtained for the oxide. However, two angles of Gruhl and Wasserman do agree with two of the author's to within  $0.49^{\circ}$ . The latitude which Gruhl and Wasserman gave themselves, between observed and calculated values, was noted to be as much as  $0.5^{\circ}$ .

It is interesting to compare the two smallest <u>d</u> values given by Geisler, Mallery, and Steigert with two corresponding values given for the oxide.

Finally, comparison of the values of Geisler, Mallery and Steigert with Gruhl and Wasserman shows correspondence only with one angle or  $\underline{d}$  spacing, namely 17.66° with 2.54  $\overset{\circ}{A}$ .

A much closer correspondence between the  $\underline{d}$  spacings of Geisler, Mallery and Steigert and that of CuO may be seen, Table 7.



Table 7

| G-M-S  | Cu0     |
|--------|---------|
| 2.78 A | 2.751 Å |
| 2.54 % | 2.530 A |
| 1.97 Å | 2.523 Å |
| 1.86 A | 2.323 A |
| 1.56 Å | 2.312 A |
|        | 1.959 Å |
|        | 1.866 Å |
|        | 1.778 Å |
|        | 1.714 A |
|        | 1.581 A |

This comparison leads this author to believe that the intermediate structure of Geisler, Mallery, and Steigert is not a structure of the alloy, but is in fact only CuO. This is a distinct probability, for in that portion of their report concerning the aging of their single crystals, there is no mention of corrosion or the prevention thereof.

The structure corresponding to the surface oxide was sought by using graphical methods as well as the analytical method of Ito. 33 A unit cell could not be found, but it was noted that CuO, Cu<sub>2</sub>O, and BeO could account for the majority of the twenty lines measured. The problem was ultimately abandoned, and all that can be said is that a compound of oxygen and Cu-Be exists.

<sup>33&</sup>lt;sub>Azaroff, L. V. and M. J. Buerger, op. cit., pp. 106-111.</sub>



- 5. Summary and Conclusions.
- (1) The lattice constants for the alpha and beta prime phases of the 2% Be-Cu alloy were 3.585 and 2.699 A respectively.
- (2) No intermediate structure capable of three dimensional diffraction was observed to exist during the course of precipitation in Be-Cu alloys. It is concluded that the alloy systems Cu-Be and Al-Cu age-harden in a similar manner and that no intermediate phase exists in Cu-Be which corresponds to that of theta prime in Al-Cu.
- (3) The possible existence of BeCuO<sub>2</sub>, BeCu<sub>2</sub>O<sub>2</sub>, or another compound of these three elements should be investigated further and the structure determined.
- (4) Future investigations into the process of precipitation in Cu-Be should be initiated. It is suggested that alloys of various compositions be used in order to obtain comparisons between and relating to the compositions; such as has been accomplished in the Al-Cu system. The high temperature camera used in this research offers a unique advantage in studies at elevated temperatures; that of observing changes due to time at temperature. It is recommended that this technique be used again in the future.



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